

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C08G 18/38, C08J 9/14</p>	<p>A1</p>	<p>(11) International Publication Number: WO 99/61504 (43) International Publication Date: 2 December 1999 (02.12.99)</p>
<p>(21) International Application Number: PCT/EP99/03148 (22) International Filing Date: 7 May 1999 (07.05.99) (30) Priority Data: 60/086,297 21 May 1998 (21.05.98) US (71) Applicant: HUNTSMAN ICI CHEMICALS LLC [US/US]; The Corporation Trust Company, 1209 Orange Street, Wilmington, Newcastle, DE 19801 (US). (72) Inventors: SINGH, Sachchida, Nand; 7 Rittenhouse Square, Sicklerville, NJ 08081 (US). COSTA, Joseph, Samuel, Jr.; 515 Bow Lane, Gilbertsville, PA 19525 (US). BERRIER, Rachel, Elizabeth; 2908 Saxony Drive, Mt. Laurel, NJ 08054 (US). (74) Agents: SWINNEN, Anne, Marie et al.; Huntsman Polyurethanes, Intellectual Property Dept., Everslaan 45, B-3078 Everberg (BE).</p>		<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: HYDROCARBON BLOWN RIGID POLYURETHANE FOAMS HAVING IMPROVED FLAMMABILITY PERFORMANCE</p>		
<p>(57) Abstract</p> <p>Rigid polyurethane or urethane modified polyisocyanurate foams having improved flame resistance are disclosed. The foams are prepared from a composition containing (a) an isocyanate, (b) an isocyanate reactive composition, (c) a hydrocarbon/water blowing agent and (d) a phosphorus material.</p> <p style="text-align: center;">Best Available Copy</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NZ	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**HYDROCARBON BLOWN RIGID POLYURETHANE
FOAMS HAVING IMPROVED FLAMMABILITY PERFORMANCE.**

BACKGROUND OF THE INVENTION

5 The present invention relates to closed cell rigid polyurethane or urethane-modified polyisocyanurate foams having improved flammability performance and blown with hydrocarbon blowing agents in combination with a minor amount of water. The invention includes the process used to produce the foams, novel compositions useful in said process and the foams prepared thereby.

10 Rigid polyurethane foams have many known uses, such as in building materials and thermal insulation. Such foams are known to have excellent flammability performance, outstanding initial and long term thermal insulation and superior structural properties.

 Rigid polyurethane foams have conventionally been prepared by reacting
15 appropriate polyisocyanate and isocyanate-reactive compositions in the presence of a suitable blowing agent. With regard to blowing agents, chlorofluorocarbons (CFC's) such as trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) have been used most extensively as they have been shown to produce foams having low flammability, good thermal insulation properties and excellent dimensional
20 stability. However, in spite of these advantages, CFC's have fallen into disfavor, as they have been associated with the depletion of ozone in the earth's atmosphere, as well as possible global warming potential. Accordingly, the use of CFC's has been severely restricted.

 Hydrochlorofluorocarbons (HCFC's) such as chlorodifluoromethane
25 (HCFC-22), 1-chloro-1,1-difluoroethane (HCFC-142b), and particularly 1,1-dichloro-1-fluoroethane (HCFC-141b) have been considered a viable interim solution. However, HCFC's have also been shown to cause a similar depletion of

ozone in the earth's atmosphere and accordingly, their use has also come under scrutiny. In fact, the widespread production and use of HCFC-141b is presently scheduled to end by the year 2002.

Therefore, there has existed a need to develop processes for the formation of rigid polyurethane foams which utilize blowing agents having a zero ozone depletion potential and which still provide foams having low flammability, good thermal insulation properties and excellent dimensional stability.

A class of materials which have been investigated as such blowing agents include various hydrocarbons such as n-pentane, n-butane and cyclopentane. The use of such materials is well-known and disclosed, e.g., in U.S. Patent Nos. 5,096,933, 5,444,101, 5,182,309, 5,367,000 and 5,387,618. Hydrocarbons offer many advantages such as zero ozone depletion potential, a very low global warming potential, low cost and are liquid at room temperature. One disadvantage of hydrocarbons however is their inherent flammability.

Rigid polyurethane foams used in building construction industry are closed cell in order to trap the blowing agent and benefit from its lower thermal conductivity, i.e., heat insulation capability. But presence of this trapped flammable gas in the cell presents a special challenge in terms of flammability performance of the closed celled foam. Though flammability of such foam has been a concern in general, surface burning characteristics of foam has been of particular concern.

Surface burning characteristics of materials are determined by test methods such as American Society of Testing Materials (ASTM) E 84 "Standard Test Method for Surface Burning Characteristics of Building Materials." It is used to assess the spread of flame on the surface of a material. Popularly known as "Tunnel test," E84 exposes a 24 ft. long by 20 inches wide foam specimen to a controlled air flow and flaming fire exposure, adjusted so as to spread a flame along the entire length of a select grade oak specimen in 5.5 minutes. Generally the test is performed on core foam of chosen thickness but on occasion it is performed on faced products. Flame

spread and smoke density are the two parameters measured in the test. The Flame Spread Index (FSI) takes into account both the rate and total distance of the propagation of a flame front, measured visually. The smoke factor is a time-integrated measurement of the occlusion of a visible beam of light. Material performance is put into categories namely 0-25 flame spread index is class I, 26-75 is class II, 76-225 is class III. Smoke limit of 450 is required in each of these classes. ASTM E 84 also has a number of other designations, such as Underwriters Laboratories 723, National Fire Prevention Association 255, or International Conference of Building Officials 8-1.

10 Since polyurethane foam laminates are used in building construction, it must adhere to the local building code requirement for flammability. When regulating materials, many of the model building codes [such as Building Officials and Code Administrators International Inc. (BOCA), International Conference of Building Officials (ICBO) and Southern Building Code Congress International Inc. (SBCCI)]
15 and insurance rating organizations [such as Underwriters Laboratories (UL); Factory Mutual Research Corporation (FMRC)] refer to quality standards developed by standards-setting organizations such as ASTM. Generally the codes require that the foam core have a flame spread index of 75 or less and a smoke development rating of 450 or less, i.e., meet Class II rating in accordance to ASTM E 84. The rigid
20 polyurethane based laminate boardstock used in the building insulation applications has exceeded this requirement and have historically been rated as Class I in the ASTM E-84 flammability test. Thus HCFC-141b blown foam currently used in the market place or CFC-11 blown foam used prior to 1993 phaseout of CFCs have been Class I.

25 A widely used method to improve the flammability performance of hydrocarbon blown closed cell rigid foam has been to add water to the formulation which when reacted with isocyanate releases carbon dioxide. This reduces the amount of hydrocarbon trapped in the closed cells of the foam. Adding water and

thus reducing hydrocarbon has deleterious effects on foam's insulation properties and its structural properties, especially at low density. Use of water reduces the amount of low thermal conductivity gas (i.e. hydrocarbon as opposed to carbon dioxide) in the closed cells of the foam. This is not desirable as a key attribute of 5 closed cell rigid polyurethane foam is its good insulation properties and good structural properties all at low densities.

Other attempts to improve the flammability performance in general and surface burning characteristics in particular of hydrocarbon blown closed cell rigid foam has centered around adding a halogenated blowing agent (e.g., US 5384338; 10 US 5385952; US 5420167, and US 5556,894) to the foam formulation. Such attempts have met with limited success. Known methods for producing foams using hydrocarbon as blowing agent and reaction systems used in such methods have not been found to produce rigid polyurethane foams having good flammability performance, in particular class I rating in ASTM E 84 test, and commercially 15 attractive thermal and structural properties at densities which are sufficiently low to make their use feasible. In short, the flammability performance associated with such hydrocarbon blown foams have generally been inferior to CFC and HCFC blown foams.

Accordingly, there remains a need for a process for the production of closed 20 celled rigid polyurethane or urethane-modified polyisocyanurate foam which utilizes hydrocarbon blowing agent with minor amount of water and which provides foams having good flammability performance, in particular class I rating in ASTM E 84 test.

It is an object of the present invention to provide closed celled rigid 25 polyurethane or urethane-modified polyisocyanurate foams blown with hydrocarbons which have good thermal insulation and structural properties along with the improved fire properties.

It is another object of the present invention to provide closed celled rigid polyurethane or urethane-modified polyisocyanurate foams blown with hydrocarbon which provides the above fire, insulation and structural properties at low densities (comparable to those used for CFC or HCFC blown foam) using minimal amounts of halogens. Lower halogen levels enhance the environmental acceptability of the foam.

SUMMARY OF THE INVENTION

It has now been found that closed cell rigid polyurethane or urethane-modified polyisocyanurate foams having excellent flammability performance and good thermal and structural properties can be obtained by using the following formulation:

- 1) an organic polyisocyanate,
- 2) a blowing agent comprising
 - (a) a hydrocarbon
 - 15 (b) water in an amount greater than 0 but less than or equal to 1.0% by weight, based on total weight of foam-forming reaction mixture
- 3) a polyfunctional isocyanate-reactive composition and
- 4) a phosphorous compound.

20 In order to produce the desired foams the amount of elemental phosphorus or organo-phosphorous compounds used is such that the amount of phosphorous is between 0.3 to 2% by weight and there is no more than 1.5% halogen, all based on the total weight of the foam forming reaction mixture.

Closed cell rigid polyurethane or urethane-modified polyisocyanurate foam
25 made with the above composition meets class I rating, i.e. flame spread index less

than or equal to 25 and smoke density of 450 or less, when subjected to ASTM E 84 testing.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a process and composition for the production of closed cell rigid polyurethane or urethane-modified polyisocyanurate foam having excellent flammability performance and good thermal and structural properties.

5 These foams are obtained by using the following formulation. The composition comprises:

- 1) an organic polyisocyanate,
- 2) a blowing agent comprising
 - (a) a hydrocarbon and,
 - 10 (b) water in an amount greater than 0 but less than or equal to 1.0% by weight, based on the total weight of foam-forming reaction mixture
- 3) a polyfunctional isocyanate-reactive composition and
- 4) a phosphorous compound

15 wherein the amount of phosphorous compound used is such that the amount of phosphorous is between 0.3 to 2% by weight and there is no more than 1.4% halogen, all based on the total weight of the foam forming reaction mixture.

Closed cell rigid polyurethane or urethane-modified polyisocyanurate foam made with the above composition meets class I rating, i.e. flame spread index less
20 than or equal to 25 and smoke density of 450 or less, when subjected to ASTM E 84 testing.

A detailed description of the components used in this invention is given below in the same order as the composition specified above.

(1) **Organic polyisocyanate:** Organic polyisocyanates suitable for use
25 in the present invention include any of the polyisocyanates known in the art for the production of rigid polyurethane or urethane-modified polyisocyanurate foams. In

particular, useful organic polyisocyanates include those having a functionality equal to or greater than 2.0 such as diphenylmethane diisocyanate (MDI) in the form of its 2,4'- and 4,4'-isomers and mixtures thereof, mixtures of diphenylmethane diisocyanate and oligomers thereof (known as "crude" MDI) and polymeric MDI 5 (i.e., polymethylene polyphenylene polyisocyanates). Polyisocyanates modified with various groups containing ester groups, urea groups, biuret groups, allophanate groups, carbodiimide groups, isocyanurate groups, uretdione groups and urethane groups may also be used in the process of the present invention. Such modified isocyanates and methods for their preparation are known in the art.

10 (2a) **Hydrocarbon blowing agent:** One or more hydrocarbon blowing agents which are vaporizable under foam forming conditions may be used. Suitable hydrocarbons include butane, isobutane, isopentane, n-pentane, cyclopentane, 1-pentene, n-hexane, iso-hexane, 1-hexane, n-heptane, isoheptane, and mixtures thereof. Preferably the hydrocarbon blowing agent is isopentane, n-pentane, 15 cyclopentane or mixtures thereof.

The hydrocarbon blowing agent should be used in an amount of from about 2 % to about 20 % and preferably from about 4 % to about 15 % by weight based on the weight of the entire reaction system.

Other physical blowing agents such as vaporizable non-hydrocarbons may 20 also be used in the present process in combination with the hydrocarbon blowing agents. Suitable blowing agents include 1,1,1,3,3-pentafluoropropane (HFC-245fa), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1-difluoroethane (HFC-152a), difluoromethane (HFC-32), chlorodifluoromethane (HCFC-22), and 2-chloropropane. When used, these blowing agents may be mixed into the 25 isocyanate-reactive component, the isocyanate component and/or as a separate stream to the reaction system.

(2b) **Water:** Water reacts with isocyanate under foam forming conditions to liberate CO₂. Water could be used with any of the physical blowing agents

specified in 2(a). Total amount of water is set at less than 1.0% by weight of the total foam formulation to obtain good thermal and structural performance. Preferred results are achieved when the amount of water is less than 0.35%.

The blowing agents are employed in an amount sufficient to give the resultant foam the desired density of less than 4.0 lb/cu.ft, preferably less than 3.5 lb/cu. ft., and most preferably 2.0 lb/cu. ft.

(3) Polyfunctional isocyanate-reactive compositions: The isocyanate-reactive compositions useful in the present invention include any of those known to those skilled in the art to be useful for the preparation of rigid polyurethane foams. Examples of suitable isocyanate-reactive compositions having a plurality of isocyanate-reactive groups include polyester polyols, polyether polyols and mixtures thereof having average hydroxyl numbers of from about 20 to about 1000 and preferably about 50 to 700 mg KOH/g and hydroxyl functionalities of about 2 to about 8 and preferably about 2 to about 6. Other isocyanate-reactive materials which can be used in the present invention include hydrogen terminated polythioethers, polyamides, polyester amides, polycarbonates, polyacetals, polyolefins, polysiloxanes, and polymer polyols.

Suitable aromatic polyester polyols include those prepared by reacting a polycarboxylic acid and/or a derivative thereof or an anhydride with a polyhydric alcohol, wherein at least one of these reactants is aromatic. The polycarboxylic acids may be any of the known aliphatic, cycloaliphatic, aromatic, and/or heterocyclic polycarboxylic acids and may be substituted, (e.g., with halogen atoms) and/or unsaturated. Examples of suitable polycarboxylic acids and anhydrides include oxalic acid, malonic acid, glutaric acid, pimelic acid, succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, trimellitic acid anhydride, pyromellitic dianhydride, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, endomethylene tetrahydrophthalic acid

anhydride, glutaric acid anhydride, maleic acid, maleic acid anhydride, fumaric acid, and dimeric and trimeric fatty acids, such as those of oleic acid which may be in admixture with monomeric fatty acids. Simple esters of polycarboxylic acids may also be used such as terephthalic acid dimethylester, terephthalic acid bisglycol and
5 extracts thereof.

Examples of suitable aromatic polycarboxylic acids are: phthalic acid, isophthalic acid, terephthalic acid, and trimellitic acid. Suitable aromatic polycarboxylic acid derivatives are: dimethyl or diethyl esters of polycarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, and trimellitic acid.
10 Examples of suitable aromatic anhydrides are phthalic anhydride, tetrahydrophthalic anhydride, and pyromellitic anhydride.

While the polyester polyols can be prepared from substantially pure reactant materials as listed above, more complex ingredients may be advantageously used, such as the side-streams, waste or scrap residues from the manufacture of phthalic
15 acid, phthalic anhydride, terephthalic acid, dimethyl terephthalate, polyethylene terephthalate, and the like.

The polyhydric alcohols suitable for the preparation of polyester polyols may be aliphatic, cycloaliphatic, aromatic, and/or heterocyclic. The polyhydric alcohols optionally may include substituents which are inert in the reaction, for example,
20 chlorine and bromine substituents, and/or may be unsaturated. Suitable amino alcohols, such as monoethanolamine, diethanolamine or the like may also be used. Examples of suitable polyhydric alcohols include ethylene glycol, propylene glycol, polyoxyalkylene glycols (such as diethylene glycol, polyethylene glycol, dipropylene glycol and polypropylene glycol), glycerol and trimethylolpropane. Examples of
25 suitable aromatic polyhydric alcohols are 1,4, benzene diol, hydroquinone di (2-hydroxyethyl) ether, bis (hydroxyethyl) terephthalate, and resorcinol.

There are many polyester polyols commercially available. Stepanpol® PS-2352, PS-2402, PS-3152 are some such polyols manufactured by the Stepan

Company. Terate[®] 2541, 254, 403, 203 are some such polyols, manufactured by Hoechst-Celanese Corporation,. Terol[®] 235, 235N, 250 are some such polyols manufactured by Oxid, Inc.

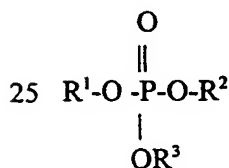
Suitable polyether polyols include reaction products of alkylene oxides, e.g.,
 5 ethylene oxide and/or propylene oxide, with initiators containing from 2 to 8 active hydrogen atoms per molecule. Suitable initiators include polyols, e.g., diethylene glycol, glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol, methyl glucoside, mannitol and sucrose; polyamines, e.g., ethylene diamine, toluene diamine, diaminodiphenylmethane and polymethylene polyphenylene polyamines;
 10 amino alcohols, e.g., ethanolamine and diethanolamine; and mixtures thereof.

Preferred initiators include polyols and polyamines.

Additional useful isocyanate-reactive materials include primary and secondary diamines (Unilink 4200), enamines, cyclic ureas, cyclic carbonate, and polycarboxylic acid. Some of these compounds react with isocyanate to evolve
 15 carbon dioxide and contribute to foam blowing.

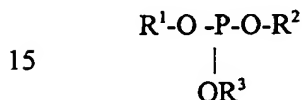
The isocyanate-reactive material is used in an amount of about 15% to about 70% and preferably about 20% to about 60% by weight of the total reaction system.

(4) Organo-phosphorous compounds: Various phosphorous containing
 20 organic compounds can be used. Suitable compounds include phosphates, phosphites, phosphonates, polyphosphates, polyphosphites, polyphosphonates, and ammonium polyphosphate. Suitable phosphate compounds are the following:



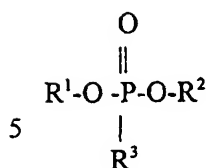
Where R¹ to R³ signifies alkyl, halogen substituted alkyl, aryl, halogen substituted aryl and cycloalkyl groups. Preferred phosphates are those where R¹ to R³ signifies C₁-C₁₂ alkyl, C₁-C₁₂ halogen substituted alkyl, phenyl, cresyl, halogen substituted phenyl and C₅-C₁₀ cycloalkyl groups. More preferred phosphates are those where R¹ to R³ signifies C₁-C₈ alkyl, C₁-C₈ halogen substituted alkyl, and phenyl groups. Most preferred phosphate compounds are those where R¹ to R³ signifies C₁-C₄ alkyl, C₁-C₄ halogen substituted alkyl, and phenyl groups. Some specific compounds under most preferred phosphates are, tributyl phosphate, tris(2-chloropropyl)-phosphate (Antiblaze 80 from Albright & Wilson), t-butylphenyl diphenylphosphate (Phosflex 71B from Akzo Nobel), triethyl phosphate (TEP from Eastman), tributyl phosphate (Phosflex 4 from Akzo Nobel), chloropropyl bis(bromopropyl) phosphate (Firemaster FM836 from Great Lakes).

Suitable phosphite compounds are the following:



Where R¹ to R³ signifies H, alkyl, halogen substituted alkyl, aryl, halogen substituted aryl and cycloalkyl groups. Preferred phosphites are those where R¹ to R³ signifies C₁-C₁₂ alkyl, C₁-C₁₂ halogen substituted alkyl, phenyl, cresyl, halogen substituted phenyl and C₅-C₁₀ cycloalkyl groups. More preferred phosphites are those where R¹ to R³ signifies, C₁-C₈ alkyl, C₁-C₈ halogen substituted alkyl, and phenyl groups. Most preferred phosphite compounds are those where R¹ to R³ signifies C₁-C₄ alkyl, C₁-C₄ halogen substituted alkyl, and phenyl groups. Some specific compounds under most preferred phosphites are triethyl phosphite (Albrite TEP from Albright & Wilson), tris(2-chloroethyl)-phosphite, triphenyl phosphite (Albrite TPP).

Suitable phosphonate compounds are the following:



Where R¹ to R³ signifies alkyl, halogen substituted alkyl, aryl, halogen substituted aryl and cycloalkyl groups. Preferred phosphonates are those where R¹ to R³ signifies C₁-C₁₂ alkyl, C₁-C₁₂ halogen substituted alkyl, phenyl, cresyl, halogen substituted phenyl and C₅-C₁₀ cycloalkyl groups. More preferred phosphonates are those where R¹ to R³ signifies C₁-C₈ alkyl, C₁-C₈ halogen substituted alkyl, and phenyl groups. Most preferred phosphonate compounds are those where R¹ to R³ signifies C₁-C₄ alkyl, C₁-C₄ halogen substituted alkyl, and phenyl groups. Some specific compounds under most preferred phosphonates are diethyl ethyl 15 phosphonate (Antiblaze 75 or Amgard V490 from Albright & Wilson), dimethyl methyl phosphanate (Amgard DMMP), bis(2-chloroethyl), 2-chloroethyl phosphonate. Especially preferred results are obtained when one of these preferred phosphonates are included in the composition.

Illustrative examples of polyphosphate compound are Amgard V-6, a 20 chlorinated diphosphate ester, from A&W. Illustrative examples of ammonium polyphosphate [(NH₄PO₃)_n; n = about 1000] is Hostaflam AP 422 from Hoechst AG and many products from A&W.

The organo-phosphorous compounds used in the invention may have one or more isocyanate-reactive hydrogens being hydroxyl groups, amino groups, thio 25 groups, or mixtures thereof. Suitable compounds include monomeric or oligomeric phosphates, phosphites, and phosphonates polyols. Suitable isocyanate-reactive phosphate compounds are those prepared by (1) the reaction of polyalkylene oxides with (a) phosphoric acids (b) partial esters of phosphoric acids; (2) the reaction of

aliphatic alcohols with (a) phosphoric acids (b) partial esters of phosphoric acids; and (3) by transesterification of products of (1) and (2). The preferred compounds include tributoxyethyl phosphate [Phosflex T-BEP from Akzo]; oligomeric organophosphate diol [Hostaflam TP OP 550 from Hoechst AG]; ethoxylated
5 phosphate esters [Unithox X-5126 from Petrolite]; mono- and diesters of phosphoric acid and alcohols [Unithox X-1070 from Petrolite].

Suitable isocyanate-reactive phosphite compounds are those prepared by (1) the reaction of polyalkylene oxides with (a) phosphorous acids (b) partial esters of phosphorous acids; (2) the reaction of aliphatic alcohols with (a) phosphorous acids
10 (b) partial esters of phosphorous acids; and (3) by transesterification of products of (1) and (2).

Suitable isocyanate-reactive phosphonate compounds are those prepared (1) by the reaction of polyalkylene oxides with phosphonic acids, (2) by the reaction of phosphite polyols with alkyl halides; (3) by the condensation of dialkyl
15 phosphonates, diethanolamine and formaldehyde; (4) by transesterification of products of (1) (2) and (3); and (5) by reaction of dialkyl alkyl phosphonate with phosphorous pentaoxide and alkylene oxide. The preferred compounds include diethyl N, N-bis(2-hydroxyethyl) aminoethyl phosphanate [Fyrol 6 from Akzo]; hydroxyl containing oligomeric phosphonate [Fyrol 51 from Akzo]

20 Elemental phosphorous can also be used.

The amount of said organo-phosphorous compound used is such that the amount of phosphorus is between 0.3 to 2% by weight and if the compound contains halogen there is no more than 1.4% halogen, based on the total weight of the foam forming reaction mixture. Preferred amount of phosphorous is between 0.4 to 1.5%
25 and most preferred is 0.5 to 1.0% by weight, based on the total weight of the foam forming reaction mixture. Also preferably there is no more than 1.25% and most preferred no more than 1.0% by weight of halogens, based on the total weight of the foam forming reaction mixture.

(5) Additives: One or more other auxiliaries or additives conventional in formulations for the production of rigid polyurethane and urethane-modified polyisocyanurate foams may be included in the reaction system. Such optional additives include, but are not limited to: crosslinking agents, foam-stabilising agents or surfactants, catalysts, infra-red opacifiers, cell-size reducing compounds, viscosity reducers, compatibility agents, mold release agents, fillers, pigments, and antioxidants. The various auxiliary agents and additives as needed for a particular purpose are generally added to the isocyanate reactive composition. Suitable auxiliaries and additives include crosslinking agents, such as triethanolamine and glycerol; foam stabilizing agents or surfactants, such as siloxane-oxyalkylene copolymers; oxyethylene-oxyalkylene copolymer; catalysts, such as tertiary amines, (e.g., dimethylcyclohexylamine, pentamethyldiethylenetriamine, 2,4,6-tris(dimethylaminomethyl) phenol, triethylenediamine); organometallic compounds (e.g., potassium octoate, potassium acetate, dibutyl tin dilaurate), quaternary ammonium salts (e.g., 2-hydroxypropyl trimethylammonium formate) and n-substituted triazines (N, N', N''-dimethylaminopropylhexahydrotriazine); viscosity reducers such as propylene carbonate, 1-methyl-2-pyrrolidinone, halogenated hydrocarbons; infra-red opacifiers such as carbon black, titanium dioxide, metal flakes; cell-size reducing compounds such as inert, insoluble fluorinated compounds, perfluorinated compounds; reinforcing agents such as glass fibers, ground up foam waste; mold release agents, such as zinc stearate; antioxidants, such as butylated hydroxy toluene; and pigments such as azo-/diazo dyestuff, phthalocyanines.

The amount of such additives is generally between 0.1-20%, preferably between 0.3-15% and most preferably between 0.5-10%, by weight based on 100% of the total foam formulation.

In operating the process for making rigid foams according to this invention, the known one-shot, prepolymer or semi-prepolymer techniques may be used

together with conventional mixing methods including impingement mixing. The rigid foam may be produced in the form of slabstock, mouldings, cavity filling, sprayed foam, frothed foam or laminates with other material such as paper, metal, plastics, or wood-board.

5 The various aspects of this invention are illustrated, but not limited by, the following examples. Unless otherwise noted, all temperatures are expressed in degrees Celsius and all formulation components are expressed in parts by weight.

EXAMPLES

The following materials are used in the examples.

10 Terate[®] 254: An aromatic polyester polyol of hydroxyl value 235 mg KOH/g, average functionality of around 2 and viscosity of 2,500 cPs @ 25°C available from Hoechst Celanese Corporation.

 Pelron[®] 9540A: Potassium octoate in diethylene glycol available from Pelron Corp.

15 Dabco[®] TMR-2: N-(2-hydroxypropyl)-N-trimethylammonium formate in dipropylene glycol available from Air Products.

 Polycat[®] 5: Pentamethyldiethylenetriamine available from Air Products.

 Polycat[®] 8: Dimethycyclohexylamine available from Air Products.

 Polycat[®] 41: An amine catalyst available from Air Products.

20 Tegostab[®] B8469: A silicone surfactant available from Goldschmidt Corporation.

 Cyclopentane: Available from Exxon Chemical Company and having purity >95%.

 Isopentane: Available from Phillips Chemical Company and having purity
25 >97%.

 TCPP: Tri(beta-chloropropyl)phosphate (% P = 9.5) available from many companies including Akzo Nobel Chemical Inc.

Antiblaze[®]75: Diethylethylphosphonate (DEEP, %P = 18.7) available from Albright & Wilson Americas. Inc. under the tradename .

Great Lakes DE-60F[™] Special: Pentabromodiphenyl oxide / aromatic phosphate available from Great Lakes Chemical Corporation.

5 Rubinate[®] 1850: A high functionality polymeric MDI available from ICI Americas.

Rigid polyurethane foam laminate boards were prepared using the formulations shown in Table 1. Laminate board samples were made on an OMS laminator. The laminator is 24.3 feet (7.4 meters) long and can produce boards up to 10 39 inches (1 meter) wide and 7.9 inches (20 centimeters) thick. The conveyor can be heated to 158°F and the laydown table to 122°F. The output is 16-33 pounds per minute. All laminates were made to a thickness of 1.5 inches and 39 inches wide, using typical black glass facer from GAF corporation. .

The processing conditions for making the laminates are shown in the 15 following Table.

Table: Laminator conditions

Laydown Table (°F)	Room Temperature
Laminator Top (°F)	140
Laminator Bottom (°F)	149
Chemicals (Tank Temperature) (°F)	82
Number of Streams	5

The foam core density was measured following ASTM D 1622. The closed cell content was measured following ASTM D2856.

Fire performance was tested on 1.3" foam taken from the core of the laminates 20 using the ASTM E 84 test method.

Thermal properties of the foam laminates were measured according to the procedures set forth in ASTM C 518. Thermal aging was performed at room temperature on the full thickness laminate. In thermal property evaluations, the lower the k-factor, the better the insulation performance of the foam.

5 The structural performance of the foam was measured on foams taken from core of the laminates. The low temperature dimensional stability was measured after 7 days of exposure at -25°C following the "Dimvac method" described in *"Techniques to Assess the Various Factors Affecting the Long Term Dimensional Stability of Rigid Polyurethane Foam," Proceedings of the Polyurethane 1995*
10 *Conference, Page 11 (1995)*. The dimensional stability of the foam was measured after 14 days exposure at 158°F / 97% RH following ASTM D2126. In dimensional stability test, the closer the % linear change is to zero, the better the dimensional performance of the foam.

Structural property of the foam is also characterized by compressive strength
15 measurements. They were measured parallel to rise and perpendicular to rise (in both machine and cross-machine directions) following the ASTM D1621, Procedure A. Generally, higher the compressive strength, better the structural performance of foam.

Foams #1, #4 and #6 represent foams prepared using the formulations
20 according to this invention. All foams were blown with hydrocarbon as the blowing agent with additional blowing from water plus isocyanate reaction.

Foams #1 and #4 which have a density of 1.8 and 1.7 pcf respectively were rated as Class I in the ASTM E-84 tests and had thermal and structural properties as good as foam #2, #3 and #5 which were rated as Class II in the ASTM E-84 test.
25 Similarly Foam #6 which was blown with essentially hydrocarbon and very little water still was rated as Class I in the ASTM E-84 tests and had thermal properties as good as foam #2, #3 and #5 which were rated as Class II in the ASTM E-84 test.

By comparison Foams #2, #3 and #5 do not come within the scope of this invention and do not meet the Class I rating in accordance with ASTM E-84.

Table 1

Samples, % of total foam	#1	#2	#3	#4
Terate [®] 254	25.53	25.53	25.53	29.14
Dabco [®] TMR-2	1.00	1.00	1.00	1.00
Pelron [®] 9540a	0.58	0.58	0.58	0.58
Polycat [®] 5	0.04	0.04	0.04	0.04
Tegostab [®] B8469	0.61	0.61	0.61	0.61
Cyclopentane	3.98	3.98	3.98	3.98
Isopentane	2.69	2.69	2.69	2.69
Water	0.15	0.15	0.15	0.15
Rubinate [®] 1850	61.06	61.07	61.07	57.46
Fire retardants				
TCPP	2.88	4.32	2.88	2.88
Antiblaze [®] 75	1.44	0	0	1.44
Great Lakes DE-60F [™] Special	0	0	1.44	0
% Phosphorous	0.543	0.410	0.302	0.543
% halogen	0.936	1.404	1.685	0.936
Isocyanate Index	325	325	325	275
Closed cell content	90	91	91	90
Foam core density, pcf	1.8	1.8	1.75	1.7
Flammability Performance in ASTM E-84 *				
Class I or II	I	II	II	I
Flame spread index	25	35	40	25
Smoke density	65	50	45	70
Thermal Properties of Laminate:				
k-factor in BTU.in/ft ² .hr.°F				
Initial	0.148	0.150	0.149	0.147
After 2 months at room temperature	0.167	0.167	0.166	0.163

	#1	#2	#3	#4
Samples, % of total foam				
Structural Properties of Foam:				
Dimensional stability, % linear change				
Dimvac at -25°C,	-0.65	-0.3	-0.35	-0.25
Dim stab at 70°C, 97% RH	1.35	0.75	0.6	0.75
Compressive Strength, psi				
Parallel to rise	17.5	18.1	18.2	14.6

What is claimed is:

1. A reaction system for the production of rigid polyurethane or urethane modified polyisocyanurate foams comprising.
 - A. an organic polyisocyanate
 - 5 B. An isocyanate reactive composition containing a plurality of isocyanate reactive groups.
 - C. A blowing agent comprising a hydrocarbon and water wherein the amount of water is less than or equal to 1.0% by weight based on the total weight of the reaction system.
 - 10 D. A phosphorous material selected from the group consisting of organo phosphorus compounds and elemental phosphorus wherein the amount of material used is such that the amount of phosphorus in the composition is equal to from about 0.3 to about 2% by weight based on the total weight of the reaction system and if an organo phosphorus compound containing halogen is used there is
15 no more than 1.4% by weight halogen based on the total weight of the reaction system.
2. A reaction system, as claimed in claim 1 wherein the organic polyisocyanate is polyphenylene polymethylene polyisocyanate.
3. A reaction system as claimed in claim 1, wherein the isocyanate-reactive
20 composition is selected from the group consisting of polyether polyols, polyester polyols and mixtures thereof having average hydroxyl numbers of from about 100 to about 1000 KOH/g and hydroxyl functionalities of from about 2 to about 8.
4. A reaction system as claimed in claim 1 wherein the hydrocarbon in the blowing agent is selected from the group consisting of butane, isobutane, isopentane,

n-pentane, cyclopentane, 1-pentene, n-hexane, iso-hexane, 1-hexane, n-heptane, isoheptane, and mixtures thereof.

5. A reaction system as claimed in claim 1 wherein the amount of water in the blowing agent is less than or equal to 0.35% by weight based on the total weight of the reaction system.

6. A reaction system as claimed in claim 1 wherein the phosphorus material is an organophosphorus compound selected from the group consisting of phosphates, phosphites, phosphonates, polyphosphates, polyphosphites, polyphosphonates, and ammonium polyphosphate.

10 7. A process for the production of rigid polyurethane or urethane modified polyisocyanurate foams, said process comprising reacting.

A. an organic polyisocyanate.

B. An isocyanate reactive composition containing a plurality of isocyanate reactive groups.

15 C. A blowing agent comprising a hydrocarbon and water wherein the amount of water is less than or equal to 1.0% by weight based on the total weight of the reaction system.

D. A phosphorous material selected from the group consisting of organo phosphorus compounds and elemental phosphorus wherein the amount of material used is such that the amount of phosphorus in the composition is equal to from about 0.3 to about 2% by weight based on the total weight of the reaction system and if an organo phosphorus compound containing halogen is used there is no more than 1.4% by weight halogen based on the total weight of the reaction system.

25 8. A rigid polyurethane or urethane modified polyisocyanurate foam prepared from the reaction system of claim 1.

WO 99/61504

PCT/EP99/03148

SPECSJMS\50593.SAM

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/03148

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G18/38 C08J9/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 12758 A (IMPERIAL CHEMICAL INDUSTRIES) 2 May 1996 (1996-05-02) page 1, line 20 -page 6, line 19; claims 1-12,21-24; tables 1,6	1-8
X	US 5 470 501 A (FISHBACK ET AL) 28 November 1995 (1995-11-28) column 1, line 52 -column 12, line 12; claims 1-12; examples	1-8
X	EP 0 770 642 A (BASF) 2 May 1997 (1997-05-02) page 2, line 8 -page 7, line 10; claim 1; example 2	1-8
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

8 October 1999

Date of mailing of the international search report

28/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5816 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bourgonje, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/03148

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 92 16573 A (BAYER) 1 October 1992 (1992-10-01) page 3, line 9 -page 6, line 20; claims 1-6; examples</p> <p style="text-align: center;">---</p>	1-8
X	<p>DE 40 26 893 A (HÜTZEN/THANEX POLYURETHANCHEMIE) 27 February 1992 (1992-02-27) column 2, line 61 -column 6, line 7; claims; example 1</p> <p style="text-align: center;">---</p>	1-8
A	<p>EP 0 608 754 A (BAYER) 3 August 1994 (1994-08-03) page 2, line 23 -page 3, line 49; claims 1-4; examples</p> <p style="text-align: center;">---</p>	1
A	<p>EP 0 658 580 A (HOECHST) 21 June 1995 (1995-06-21) page 2, line 16 -page 5, line 55; examples</p> <p style="text-align: center;">-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Patent Application No

PCT/EP 99/03148

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9612758	A	02-05-1996	AU 691671 B	21-05-1998
			AU 3607295 A	15-05-1996
			DE 69504093 D	17-09-1998
			DE 69504093 T	21-01-1999
			EP 0787164 A	06-08-1997
			ES 2119476 T	01-10-1998
			JP 10507482 T	21-07-1998
			NZ 293596 A	28-07-1998
<hr/>				
US 5470501	A	28-11-1995	CA 2175972 A	09-11-1996
			EP 0742241 A	13-11-1996
			US 5504125 A	02-04-1996
			US 5523332 A	04-06-1996
<hr/>				
EP 770642	A	02-05-1997	US 5837742 A	17-11-1998
			US 5705823 A	06-01-1998
			CA 2188459 A	28-04-1997
<hr/>				
WO 9216573	A	01-10-1992	DE 4109076 A	24-09-1992
<hr/>				
DE 4026893	A	27-02-1992	NONE	
<hr/>				
EP 608754	A	03-08-1994	DE 4302460 A	04-08-1994
			AT 158801 T	15-10-1997
			CA 2114252 A	30-07-1994
			DE 59404177 D	06-11-1997
			ES 2107694 T	01-12-1997
			JP 2780148 B	30-07-1998
			JP 7053762 A	28-02-1995
			US 5367000 A	22-11-1994
<hr/>				
EP 658580	A	21-06-1995	DE 4342973 A	22-06-1995
			AT 182342 T	15-08-1999
			CA 2136768 A	17-06-1995
			CZ 9403175 A	12-07-1995
			DE 59408514 D	26-08-1999
			JP 7252416 A	03-10-1995
<hr/>				

This Page Blank (uspto)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

This Page Blank (uspto)